TDTS 57

Characterisation of paint samples by direct desorption TD–GC/MS

Summary

This Application Note describes the application of direct thermal desorption for the analysis and quantitation of volatile organic chemicals (VOCs) and semi-volatile organic chemicals (SVOCs) in dried and 'wet' paint samples.

Introduction

In accordance with indoor air quality guidlines, paint manufacturers regularly test the VOCs emitted from their products once applied to a surface and cured. However, in addition to this, some manufacturers also wish to determine the VOC and SVOC content of either the raw materials or final product, as this information is complementary to emissions tesing in terms of assessing the potential for toxic or harmful compounds to be released over time.

Direct thermal desorption of materials is ideally suited to this type of sample introduction, and it allows selective pre-concentration of the compounds of interest prior to analysis by GC(MS). Direct desorption can be carried out on both the water-based paint and dried paint flakes, to evaluate the VOC content in the raw material and the residual VOCs retained by the cured product respectively.

Preparation of paint samples for direct desorption

There are a number of considerations to be made when carrying out direct desorption of materials.

- Because relatively small amounts of sample are used in this technique (typically milligrams), the sample must be sufficiently homogeneous that this amount of sample can be considered as representative of the whole sample.
- Ideally, the sample should not have a significant water content
- The sample should have a relatively high surface area/mass ratio (other materials suited to direct desorption include powders, resins and adhesives, as discussed in Application Note TDTS 9).

Typically, the sample is inserted into an empty thermal desorption tube and secured by plugs of glass wool (ideally the sample should be inserted into a PTFE liner, which can be removed from the tube after use, thus reducing the extent of tube cleaning required). In the case of 'wet' paint samples, a small amount of the sample is weighed, smeared onto the inside of the PTFE liner, and inserted into an empty tube ready for desorption, as illustrated in Figure 1. A small bed of sorbent can be used at the front of the tube, acting as a filter to prevent any high-boiling sample matrix entering the sample flow path. It is important to ensure that the sample is contained within the heated zone of the tube and also to avoid blocking the tube, which would prevent efficient carrier gas flow through the sample, potentially reducing the extraction efficiency.

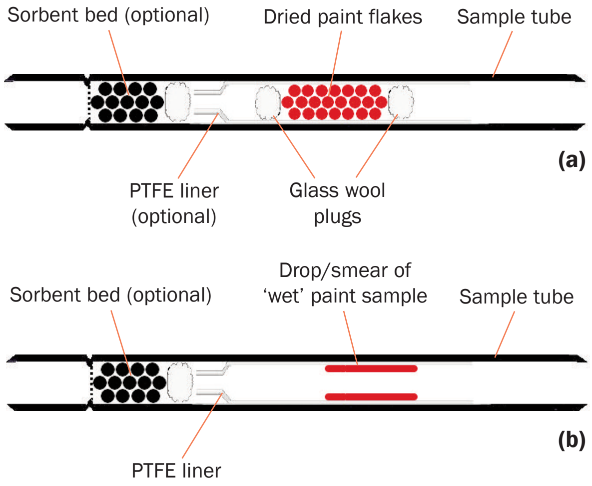

Figure 1: An illustration of sample preparation for direct desorption of (a) dried paint flakes; (b) 'wet' paint.

The advantage of direct desorption over other sampling techniques is the minimal sample preparation. Solvent extraction typically involves numerous extraction processes, which can be time-consuming, whereas direct desorption only requires the analyst to load the sample into the tube (all other steps being carried out by the automated thermal desorption system).

Sensitivity is greatly improved relative to standard solvent extraction techniques, with no masking of peaks by large solvent injections, and no concerns over the extraction efficiency of the solvent. The SecureTD-Q™ facility offered by all Markes' thermal desorption systems also addresses one of the issues which previously may have favoured solvent extraction – the ability to re-analyse the same sample. SecureTD-Q overcomes the 'one-shot' limitation of thermal desorption, by re-collection of the sample, allowing repeat analysis for method development and validation of the analytical procedure.

Experimental

TD:

Prepurge:	1 min, split on, trap in-line
Tube desorption:	10 min at 300 °C (for calibration solution on Tenax® TA), split on; 10 min at 200 °C (direct desorption of paint sample), split on
Focusing trap:	General-purpose (U-T2GPH)
Trap conditions:	–10 °C, heated to 300 °C for 3 min at maximum heating rate, split on
Flow path:	200 °C
Desorb flow:	20 mL/min
Split flow:	100 mL/min
Column flow:	2 mL/min

GC/MS:

Column:	30 m × 0.25 mm × 0.25 µm DB-1MS
GC program:	50 °C start, 10 °C/min to 250 °C, hold for 2 min
MS source:	230 °C
MS aux.:	280 °C
MS quad:	150 °C
Scan range:	35–350 amu

Results and discussion

1. Direct desorption of dried paint flakes

When carrying out any quantitative measurements using direct desorption, it is important to ensure that the method used allows complete extraction and recovery of the compounds of interest from the sample matrix during the primary desorption step. The example below illustrates the desorption of a 2 mg paint flake, which was placed into an empty thermal desorption tube and heated to 220 °C to extract the residual volatiles from it. After the inital analysis, repeat desorption of the sample was carried out, to evaluate the desorption efficiency.

Figure 2 shows that this method gave complete recovery of the compounds of interest, thus demonstrating its suitability for quantitative measurement of the VOCs in the paint.

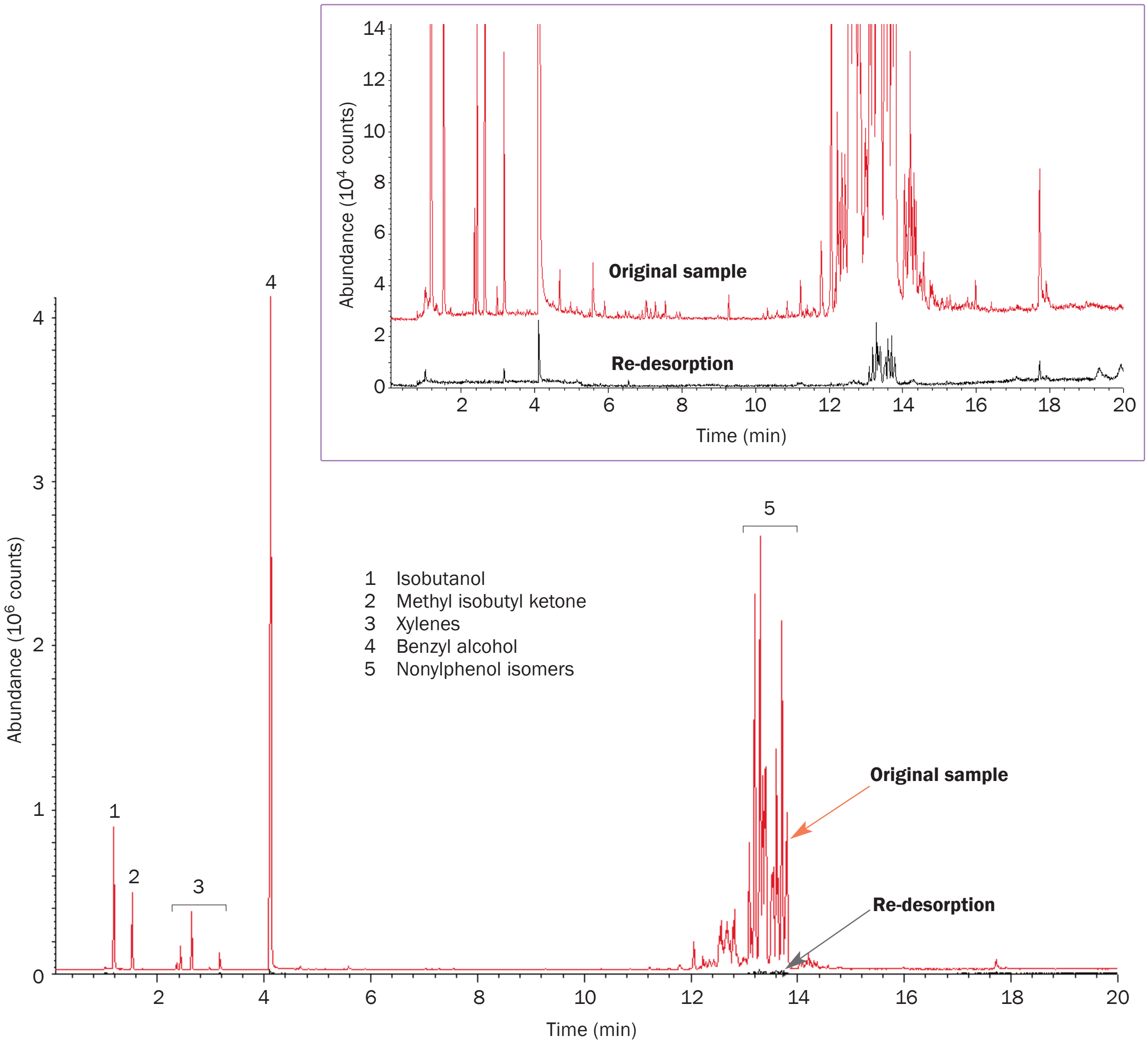

Figure 2: Direct desorption of a 2 mg paint flake at 220 °C. Re-desorption of the sample demonstrates minimal carryover (see expansion of baseline in inset).

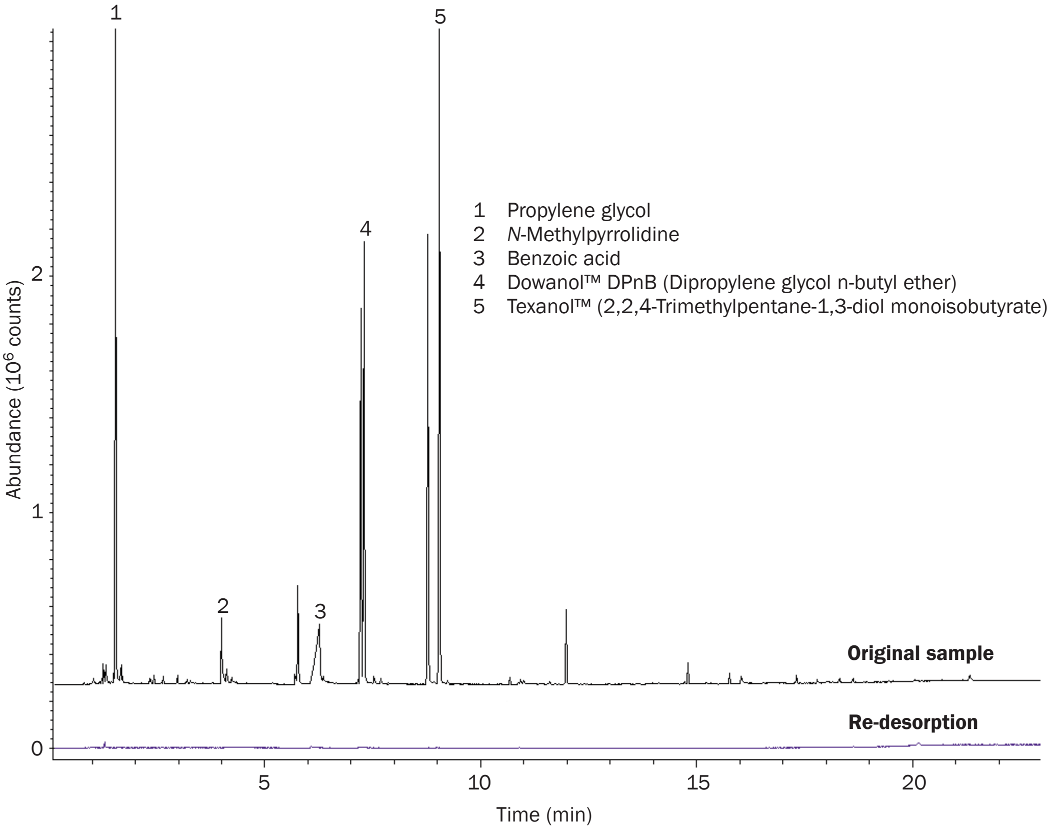

Figure 3: Direct desorption of 3.3 mg of water-based paint at 200 °C, followed by repeat desorption to demonstrate no carryover.

2. Direct desorption of water-based paint for quantitative VOC measurement

In order to carry out quantitative measurement of the VOCs contained in the water-based paint, it was again important to establish that the direct desorption technique facilitated complete recovery of the compounds of interest. Samples were prepared by weighing a known amount of paint into a PTFE liner and desorbing them inside a thermal desorption tube at 200 °C. This was then followed by a repeat desorption of the same sample. Figure 3 displays the results of the initial and repeat desorptions, and illustrates that the first direct desorption is sufficient to fully extract the compounds of interest from the sample matrix.

In order to quantify the levels of VOCs present in the paint sample, a standard solution of the compounds of interest was prepared in methanol and loaded onto a sorbent tube packed with Tenax TA using a Calibration Solution Loading Rig (CSLR™). The methanol was allowed to purge from the tube for approx 3 minutes before removing the tube from the loading rig. More information on calibration methods for thermal desorption can be found in Application Note TDTS 7.

The tubes were then desorbed at 300 °C, giving the calibration curves shown in Figure 4. Calibration data were then used to determine the quantities of propylene glycol, Dowanol™ DPnB and Texanol™ in the paint sample. Results are displayed in Table 1.

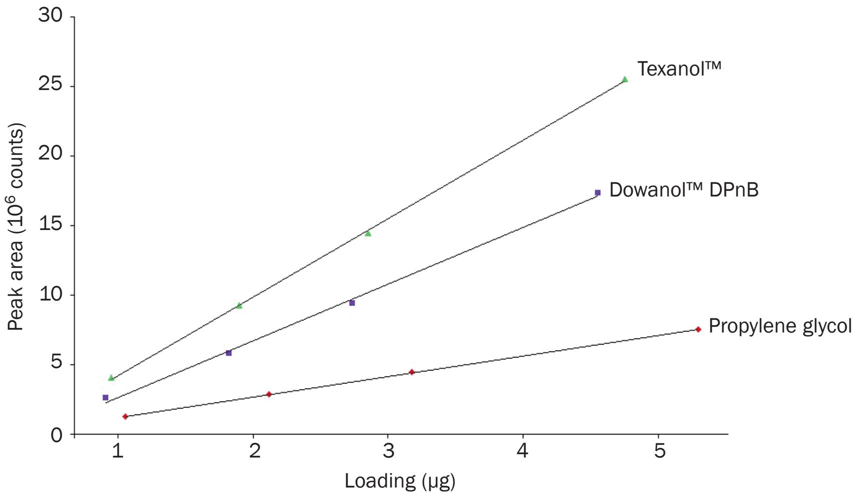

Figure 4: Calibration curves for quantitation of VOCs in water-based paint.

Sample weight (mg)	Propylene glycol			Dowanol™ DPnB			Texanol™		
	Peak area	Amount (µg)	Amount (w/w %)	Peak area [a]	Amount (µg)	Amount (w/w %)	Peak area [a]	Amount (µg)	Amount (w/w %)
3.3	39.47	39.7	1.20	52.01	52.36	0.16	74.28	74.53	0.23
8.1	123.6	123.8	1.53	142.5	142.8	0.18	186.2	186.5	0.23

Table 1: Results for quantitation of VOCs in water-based paint.
[a] Value is the sum of two isomers.

Conclusions

This Application Note demonstrates how direct desorption of both dry and wet paint samples can be used as a quantitative analytical technique for determination of the VOC content. Minimal sample preparation is required, and complete recovery of all analytes was obtained.

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Tenax® is a registered trademark of Buchem B.V., The Netherlands.

Texanol™ is a trademark of the Eastman Chemical Company, Kingsport, Tennessee, USA.

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